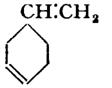
146. *The Formation of* trans-1 : 2-*Divinyl*cyclo*butane from Butadiene.*

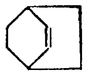
By Hugh W. B. Reed.

About 5% of *trans*-1 : 2-divinyl*cyclo*butane has been shown to be present in the products of the thermal dimerisation of butadiene, with probably a trace of octa-1 : 3 : 7-triene.

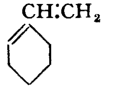
The thermal dimerisation of buta-1 : 3-diene was first investigated by Lebedev (*J. Russ. Phys. Chem. Soc.*, 1910, **42**, 949) who established, contemporaneously with Hoffmann and Tank (*Z. angew. Chem.*, 1912, **25**, 1465), the structural formula of the product as 4-vinyl*cyclo*hexene (I) (see also Lebedev and Skavvonskaya, *J. Russ. Phys. Chem. Soc.*, 1911, **43**, 1124; Lebedev, *ibid.*, 1913, **45**, 1249). Since 1930, numerous workers have described the use of various catalysts and conditions giving several other ill-defined dimeric products besides 4-vinyl*cyclo*hexene. Vaughan (*J. Amer. Chem. Soc.*, 1932, **54**, 3866) claimed the preparation of (II), but it seems very likely that this was, in fact, 4-vinyl*cyclo*hexene itself. Lebedev and Sergienko (*J. Gen. Chem. U.S.S.R.*, 1935, **5**, 1829) obtained evidence for the existence of a dimer boiling higher than 4-vinyl*cyclo*hexene, and ascribed to it the conjugated structure, 1-vinyl*cyclo*hexene (III). Slobodin (*ibid.*, p. 1415) claimed the formation of the 1 : 4-dihydro-*p*-xylene (IV) and isomers of it; more evidence for this has recently been given (Slobodin and Rachinsky, *ibid.*, 1947, **17**, 374; Slobodin, Rachinsky, and Shokov, *ibid.*, 1948, **18**, 1545), but the yields appear to be very small.



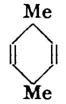
(I.)



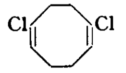
(II.)



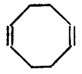
(III.)



(IV.)



(V.)



(VI.)

After Brown, Rose, and Simonsen's observation (*J.*, 1944, 101) that 2-chlorobutadiene dimerises on storage to give a product containing a *cyclo*octadiene derivative which is now recognised to be 1 : 6-dichloro*cyclo*octa-1 : 5-diene (V) (Cope and Schmitz, *J. Amer. Chem. Soc.*, 1950, **72**, 3056), Foster and Schreiber (*ibid.*, 1948, **70**, 2303) and Ziegler (*Angew. Chem.* 1947, *A*., **59**, 177) demonstrated the presence of a *cyclo*octadiene in the higher-boiling material remaining after the removal of the 4-vinyl*cyclo*hexene. Characterisation of this compound as the stable *cis-cis-cyclo*octa-1 : 5-diene (VI) has been recently achieved by Ziegler and Wilms (*Annalen*, 1950, **567**, 1).

The non-catalytic thermal dimerisation of butadiene has now been shown to yield another product, identified as substantially *trans*-1 : 2-divinyl*cyclo*butane (VII). This appeared at about 110° during the distillation of the products before the 4-vinyl*cyclo*hexene and was isolated by high-efficiency fractionation of the bulked foreruns from a number of experiments. It was estimated to amount to 4—5% of the 4-vinyl*cyclo*hexene.

The presence of two ethylenic linkages was indicated by absorption of two molecules of bromine to give a liquid tetrabromide and two molecules of hydrogen to yield a fully saturated hydrocarbon, evidently *trans*-1 : 2-diethyl*cyclo*butane.

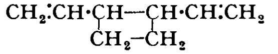
Physical constants of butadiene dimers and their hydrogenated derivatives.

trans-1 : 2-Divinyl*cyclo*butane [1]	b. p. 112—113°	n_D^{20} 1·4451	d_{20}^{20} 0·7831
4-Vinyl*cyclo*hexene [1]	b. p. 131°	n_D^{20} 1·4655	d_{20}^{20} 0·8309
*cis-cis-cyclo*Octa-1 : 5-diene [2]	b. p. 151°	n_{He}^{20} 1·4936	d_4^{20} 0·8811
,, ,, [3]	b. p. 51—52°/25 mm.	n_D^{25} 1·4910	d_4^{25} 0·8760
trans-1 : 2-Diethyl*cyclo*butane [1]	b. p. 115·5°	n_D^{20} 1·4128	—
Ethyl*cyclo*hexane [1]	b. p. 131°	n_D^{20} 1·4329	—
*cyclo*Octane [2]	b. p. 150°	n_{He}^{20} 1·4587	d_4^{20} 0·8358

[1] Reed, this work. [2] Ziegler and Wilms, *loc. cit.* [3] Cope, Stevens, and Hochstein, *J. Amer. Chem. Soc.*, 1950, **72**, 2512.

The infra-red spectrum (Fig. 2), clearly different from that of 4-vinyl*cyclo*hexene (Fig. 1) showing that none of the latter was present, was characterised by the strong absorption at 10·1 and 11μ., typical of the vinyl group. Absence of absorption bands characteristic of other types of ethylenic linkage (Thomson, *J.*, 1948, 328) indicated the probability that both double bonds were present as exocyclic vinyl groups.

Ozonolysis of the dimer in methyl acetate at −40° gave *trans-cyclo*butane-1 : 2-dicarboxylic acid, m. p. 131° (Fuson *et al.*, *J. Amer. Chem. Soc.*, 1929, **51**, 1536; 1934, **56**, 1774; Buchman, Reims, and Schlatter, *ibid.*, 1942, **64**, 2692) (diphenacyl and di-*p*-bromophenacyl ester). Further examination of the ozonolysis products after removal of the *trans-cyclo*butane-1 : 2-dicarboxylic acid led to the isolation of a small amount of succinic acid (diphenacyl and di-*p*-bromophenacyl esters); no isomeric *cyclo*butanedicarboxylic acid was found. Although the high volatility of the hydrocarbon and its ready autoxidation resulted in some loss during ozonolysis, it is concluded that it consisted mainly of the *cyclo*butane derivative (VII) with probably a small amount of octa-1 : 3 : 7-triene (VIII).



$\begin{array}{c}CH_2{:}CH{\cdot}CH{-}CH{\cdot}CH{:}CH_2\\ CH_2{-}CH_2\end{array}$

(VII.)

$CH_2{:}CH{\cdot}CH{:}CH{\cdot}CH_2{\cdot}CH_2{\cdot}CH{:}CH_2$

(VIII.)

Recently, certain highly substituted chlorofluoroethylenes (Henne and Ruh, *J. Amer. Chem. Soc.*, 1947, **69**, 279) and acrylonitrile (Coyner and Hillman, *ibid.*, 1949, **71**, 324) have been shown to yield *cyclo*butane derivatives by head-to-head, tail-to-tail dimerisation on heating. Dykstra (*ibid.*, 1934, **56**, 1625) and Cupary and Carothers (*ibid.*, p. 1167) had assigned *cyclo*butane structures (IX) and (X) to the dimers formed on heating of vinylacetylene and divinylacetylene respectively.

FIG. 1.

4-*Vinyl*cyclo*hexene.*

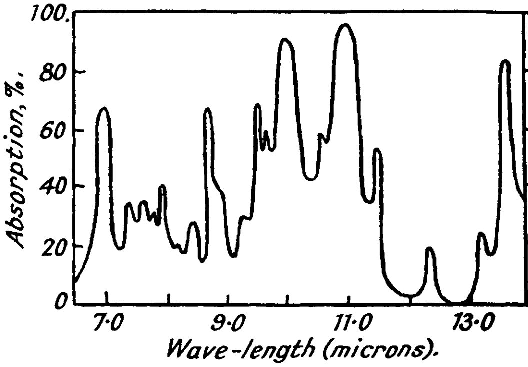
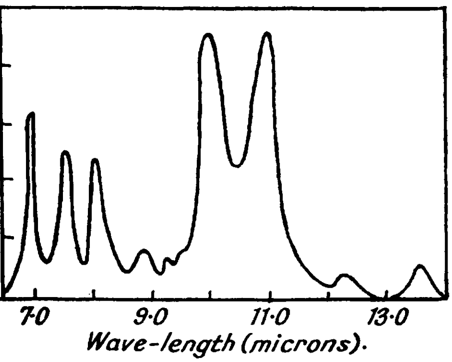
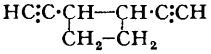


FIG. 2.

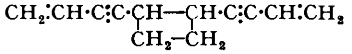
trans-1 : 2-*Divinyl*cyclo*butane.*





$\begin{array}{c}HC{:}C{\cdot}CH{-}CH{\cdot}C{:}CH\\ CH_2{-}CH_2\end{array}$

(IX.)



$\begin{array}{c}CH_2{:}CH{\cdot}C{:}C{\cdot}CH{-}CH{\cdot}C{:}C{\cdot}CH{:}CH_2\\ CH_2{-}CH_2\end{array}$

(X.)

These formulæ have been the subject of much criticism by Bergmann (*Trans. Faraday Soc.*, 1939, **35**, 1025; "The Chemistry of Acetylene Compounds," Interscience, New York, 1948, p. 81), but comparison of the physical constants of the octahydro-derivative of (IX) (b. p. *ca.* 120°, n_D^{20} 1·4270) with hydrogenated *trans*-1 : 2-divinyl*cyclo*butane, together with Cupary and Carothers's chemical evidence (*loc. cit.*), indicates that the vinyl- and divinyl-acetylene dimers undoubtedly contain at least a considerable proportion of compounds (IX) and (X) respectively.

EXPERIMENTAL.

Infra-red absorption spectra were determined with a Grubb Parsons spectrometer, the pure liquids being used in a cell of 30—50-μ. thickness.

trans-1 : 2-*Divinyl*cyclo*butane from Butadiene.*—Butadiene was heated in an autoclave at 150° for 18 hours under a pressure adjusted to 100 atmospheres with nitrogen. Oxygen was carefully excluded, and 3% of quinol used to inhibit polymerisation. The products were distilled in a 60-plate high-efficiency still and the initial fraction, b. p. <131°, was reserved. A number of these foreruns were bulked and redistilled in the same still. trans-1 : 2-*Divinyl*cyclo*butane*, b. p. 112—113°, was obtained (for physical constants see table) (Found : C, 88·9; H, 11·2%; Br no., 300. C_8H_{12} requires C, 88·9; H, 11·1%: Br no., 297).

trans-1 : 2-*Diethyl*cyclo*butane.*—The dimer (8·04 g.) was hydrogenated at room temperature and pressure in acetic acid (40 c.c.) in the presence of pre-reduced Adams's platinum oxide catalyst; 3510 c.c.

were absorbed (Calc. for two moles of hydrogen, 3570 c.c.). Filtercel was then added, and the catalyst removed by filtration and washed with ether. Ether was added to the filtrate, the acetic acid washed out, and the ethereal solution distilled, to give trans-1 : 2-*diethyl*cyclo*butane* (5·8 g.), b. p. 115·5° (see table) (Found : C, 85·7; H, 14·4. C_8H_{16} requires C, 85·7; H, 14·3%).

Ozonolysis of trans-1 : 2-*Divinyl*cyclo*butane.*—*trans*-1 : 2-Divinyl*cyclo*butane (2·54 g.) in methyl acetate (50 c.c.) was ozonised at −40°. After completion of the ozonisation, the solvent was removed *in vacuo*, and the ozonide decomposed by warming it on a water-bath with 40 c.c. of water and 3 c.c. of 30% hydrogen peroxide. After final heating of the solution for 30 minutes, the water was removed *in vacuo*. The clear oil (2·3 g.) remaining solidified completely on storage and was then taken up in ethyl acetate, and a little insoluble polymeric material removed. Benzene was added, and a crystalline solid (1·04 g.), m. p. 123—128°, obtained; recrystallisation from benzene–ethyl acetate gave pure *trans-cyclo*butane-1 : 2-dicarboxylic acid, needles, m. p. 131° (Found : C, 50·0; H, 5·6%; equiv., 72. Calc. for $C_6H_8O_4$: C, 50·0; H, 5·5%; equiv., 72). It gave the *di*-p-*bromophenacyl* ester, needles (from alcohol), m. p. 158° (Found : C, 49·1; H, 3·6. $C_{22}H_{18}O_6Br_2$ requires C, 49·1; H, 3·35%), and the *di-phenacyl* ester, needles (from alcohol), m. p. 98° (Found : C, 69·5; H, 5·4. $C_{22}H_{20}O_6$ requires C, 69·5; H, 5·3%). From the filtrate from the initial *trans-cyclo*butane-1 : 2-dicarboxylic acid, a further 0·5 g. of impure acid (m. p. 120—125°) was obtained (yielding only the diphenacyl ester, m. p. 98° above). Finally, 74 mg. of impure succinic acid, m. p. 175—178°, were obtained [di-*p*-bromophenacyl ester, plates (from methyl ethyl ketone), m. p. and mixed m. p. 211°, and diphenacyl ester, needles (from alcohol), m. p. and mixed m. p. 151°].

Authentic cyclo*Butanedicarboxylic Acids.*—*cis-cyclo*Butane-1 : 2-dicarboxylic acid, prepared by the method of Fuson *et al.* (*loc. cit.*), had m. p. 139·5° and gave the *di*-p-*bromophenacyl* ester, plates (from ethanol-acetone), m. p. 153° (Found : C, 49·2; H, 3·5%) and the *di-phenacyl* ester, needles (from alcohol), m. p. 113° (Found : C, 69·4; H, 5·3%). *trans-cyclo*Butane-1 : 2-dicarboxylic acid, prepared by isomerisation of the *cis*-acid in concentrated hydrochloric acid at 190°, was identical with the sample prepared above, as were the corresponding derivatives. *trans-cyclo*Butane-1 : 3-dicarboxylic acid, m. p. 174° (Haworth and Perkin, *J.*, 1898, **73**, 336), gave the *di*-p-*bromophenacyl* ester, needles (from ethanol), m. p. 122° (on heating from room temperature), m. p. 129° (on reheating after initial solidification) (Found : C, 49·2; H, 3·5%), and the *di-phenacyl* ester, needles (from ethanol), m. p. 100° (Found : C, 69·5; H, 5·3%).

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